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ON THE GUNNING-KJELDAHL METHOD AND A
MODIFICATION APPLICABLE IN THE
PRESENCE OF NITRATES.

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The Gunning Method (in absence of nitrates).

The modification of the Kjeldahl method, proposed by Gunning in 1889, has since been indorsed by a number of well-known chemists.

The Gunning method is very simple—the only reagents used previous to the distillation with caustic soda being sulphuric acid and potassium sulphate, the latter taking the place of the three reagents—mercury, (oxide or metallic), potassium permanganate and potassium sulphide—ordinarily used.

The mixture of sulphuric acid and potassium sulphate boils at a high temperature, and, as a rule, oxidizes the organic substance more rapidly than the ordinary mixture of sulphuric acid and oxide of mercury.

The results obtained by Gunning,* Atterberg,† Van Slyke‡ and others, including the writer, on fodders, dairy products, fertilizers free from nitrates, and various organic substances, show that this method is fully as accurate as the ordinary Kjeldahl method, and, in some cases, gives better results. It is a well known fact that the nitrogen of many alkaloids, azo-compounds and various bodies of the aromatic series cannot be determined by the usual Kjeldahl method, but Gunning and Atterberg have obtained good results on morphine, quinine, indigo and aniline oxalate by the Gunning modification.

* Fres. Zeit., **28**, 188.† Chem. Zeitung, **14**, 509.‡ U. S. Dept. Agr. Div. Chem. Bull., **31**, 142.CONN
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The chief disadvantage of the method is the frothing which occurs during the first part of the heating. This frothing, however, causes but little trouble if a flask of at least 500 c.c. capacity (which can afterwards be used for the distillation), is employed and care be taken in adjusting the heat.

The Gunning mixture is, at ordinary temperatures, half-solid, and must be heated before it can be measured for use. It is therefore best to add 18 grams of potassium sulphate and 20 c.c. of sulphuric acid, separately and in the order named, to the flask containing the substance, shaking a few times before heating. The coarsely powdered sulphate may be conveniently measured out in a cartridge-shell adjusted to hold 18 grams and provided with a wire handle. The acid may be added from a graduated cylinder or a burette of wide calibre connected by a siphon with the acid reservoir.*

After the digestion is completed water should be added before the mixture becomes too cold, otherwise it is difficult to obtain a solution of the solid mass.

The writer has found that the fertilizer-chemical known in the trade as "High Grade Sulphate of Potash," and costing but a few cents a pound, answers every purpose, and is, in fact, better than the white sulphate of the apothecary, being usually free from moisture and chlorides, the presence of which tends to increase the frothing.

Following is a comparison of results, obtained by the methods named, on those forms of organic nitrogenous matter which are most commonly used in mixed fertilizers, and on four commercial fertilizers free from nitrates.

	Kjeldahl Method.	Gunning-Kjeldahl Method
Cotton Seed Meal.....	7.06	7.11
" " ".....	7.10	7.13
" " ".....	7.10	7.15
" " ".....	6.95	6.97
Castor Pomace.....	5.56	5.59
Tankage.....	5.03	5.07
".....	5.72	5.82
Bone.....	4.03	4.02
".....	3.92	3.90
Dry Ground Fish.....	8.69	8.77
" " ".....	8.14	8.06
Peruvian Guano.....	2.88	2.95
Mixed Fertilizer†.....	3.45	3.45
" " ‡.....	3.00	3.00
" " §.....	3.80	3.76
" ".....	1.82	1.81

* Report Conn. Agl. Expt. Station, 1889, 192.

† Contains 1.89 per cent. Nitrogen in Ammonia salts.

‡ " 1.76 " " " "

§ " 1.77 " " " "

The Modified Method applicable in the presence of Nitrates.

In laboratories where fertilizer analyses are being made, the adoption of the Gunning method would tend to complicate rather than to simplify matters so long as in the presence of nitrates nitrogen is determined by another method.

It is impracticable to add salicylic acid to Gunning's reagent as such a mixture could only be used while hot and it is important that the temperature be kept as low as possible during the early stages of the digestion. It occurred to the writer, however, that Scovell's mixture of sulphuric and salicylic acids might be used in the ordinary way, potassium sulphate being added later in the process in place of mercury. After a number of unsuccessful trials—unsuccessful because too much potassium sulphate was used and the boiling point of the liquid became so high that oxides of nitrogen were driven off—the following plan was settled upon.

The material, .5 to 1.0 gram, is digested with 80 c. c. of Scovell's salicylic acid mixture (30 c. c. of sulphuric acid and 2 gms. salicylic acid) in a flask of 600 c. c. capacity, for two hours with frequent shaking. Two grams of zinc dust are then slowly added, with continual shaking, and the flask heated, at first gently, until after a few minutes boiling, dense fumes are no longer given off. Thus far the process is the same as in the Scovell-Kjeldahl method (the official method of the Association of Official Agricultural Chemists) except, that the digestion is continued for two hours, which, in some cases, the writer has found absolutely necessary in order to secure complete solution of the nitrate. Ten to twelve grams of potassium sulphate are next added and the boiling continued for a little time after the solution is colorless or, if iron is present, has a light straw color which remains unchanged. On cooling, as the mixture begins to solidify, water is added, at first slowly with shaking, and the distillation with caustic soda is carried on in the usual manner.

The trials thus far made with this method on nitrates and fertilizers containing nitrates, have proved entirely satisfactory.

In the following table are given the results obtained by the official method and the method here described, together with the percentage of nitrogen in nitrates as determined by the Schulze-Tiemann method.

The average of the 25 determinations by the Scovell-Jodlbauer method is 4.64 per cent., by the proposed method 4.65. The greatest discrepancy in any instance is one-tenth per cent., the average discrepancy five one-hundredths per cent. In ten cases the proposed method gave the lower result, in 13 cases the higher result.

	Nitrogen in Nitrates by Schulze-Tiemann.	Total Nitrogen	
		by Scorell-Jodlbauer.	by Proposed Method.
Pure Potassium Nitrate	---	18.73	18.71
Commercial Nitrate of Soda	---	15.86	15.90
Tobacco Dust	---	1.76	1.71
Mixture of Ground Bone, Muriate of Potash and Nitrate of Soda	3.61	5.74	5.66
Mixture of Bone, Tankage, Dis. Bone Black, Mur. Potash and Nitrate of Soda	1.46	3.81	3.85
Mixture of Bone, Tankage, Dis. Bone Black, Sulph. and Mur. Potash, Sulph. Am. and Nitrate Soda	.63	4.15	4.07
Mixture of Bone, Tankage, Dis. Bone Black, Sulph. and Mur. Potash and Nitrate of Soda	.43	4.03	4.10
Mixture of Tankage, Dis. Bone Black, Mur. Potash and Nitrate of Soda	2.23	4.41	4.51
Mixture of Tankage, Dis. Bone Black, Wood ashes and Nitrate of Soda	1.63	3.85	3.85
Mixed Fertilizer	.56	3.82	3.86
"	2.39	6.89	6.99
"	.69	4.84	4.89
"	1.55	3.45	3.47
"	.86	3.05	3.10
"	.86	2.70	2.65
"	1.54	3.56	3.63
"	.21	2.84	2.79
"	.83	3.69	3.76
"	.12	2.83	2.77
"	.95	4.84	4.91
"	.70	2.48	2.44
"	.68	2.56	2.56
"	.38	3.56	3.55
"	.91	2.54	2.58
"	2.91	5.02	4.96



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